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Vapor Stream Dilution by Pulse-Width Modulation

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VAPOR STREAM DILUTION BY PULSE-WIDTH MODULATION

Introduction. The ability to prepare accurate calibrated vapor samples is of profound importance in the use and development of analytical instruments for gas phase environmental monitoring. In chemical vapor sensor research, dynamic gas streams are generally preferred over static methods, especially for very dilute vapors. Dynamic methods minimize the effects of wall adsorption on vapor stream composition. A variety of methods have been developed for the generation of calibrated vapor streams (1). Typically, the vapor source is a bubbler, permeation tube, or diffusion tube. The vapor stream supplied by the source is often diluted with additional carrier gas using a flow system. A wide range of concentrations can be obtained simply by adjusting carrier gas flow rates. We have previously described an automated vapor-generation system designed for use in chemical sensor research (2).

We now wish to describe some important operating principles and methods that influence the dilution of vapor streams by a pulse-width modulation method. We became interested in this method after purchasing a VG-7000 vapor generation system from Microsensor Systems, Inc. (Springfield, VA); this instrument uses pulse-width modulation. We found that the correct operation of the pulse-width modulation dilution method requires that a critical assumption of the method be recognized and adhered to. Because we know of several other laboratories using similar vapor generation systems or other pulse-width modulation schemes, we believe it is worthwhile to discuss this assumption, and the methods we use to insure that its conditions are met. In this note we will focus only on those aspects of vapor generation system design and use that influence correct operation of the pulse-width modulation dilution method. We will not attempt to completely describe the VG7000 vapor generation system.

System Design and Dilution Method. The designs of the overall vapor generation system and various subsystems are shown in Figures 1 to 6. Each of three bubbler modules houses four bubblers which are maintained at constant temperature in a machined aluminum block with inlets and outlets for water from a refrigerated circulating water bath. We maintain the bubblers at 15°C. The method of selecting a bubbler is illustrated in Figure 2. The saturated (at 15°C) vapor stream progresses through three stages of dilution, shown in Figures 3 and 4. Finally, the output of the vapor generation instrument is either clean carrier gas for sensor baseline and recovery determination, or the diluted vapor stream for evaluation of sensor response.

Carrier gas supplied to the system at various points is regulated at each point to a single constant flow rate using electronic mass flow controllers. We use dry nitrogen regulated to 120mL/min at each point, but for the discussion in this note we will assume all flow controllers are adjusted to 100mL/min, and will loosely refer to the clean carrier gas as "air". The tubing throughout the system is 1/4" OD, 1/8" ID teflon tubing, except in carefully selected locations where smaller bore tubings are chosen to cause flow restrictions and pressure differentials.

The dilution method shown in Figures 3 and 4 consists of three pulse-width modulation stages. Each stage contains two three way solenoid valves connected by a tee junction to a mixing chamber. One valve (referred to as the vapor valve) receives a vapor stream at 100mL/min while the other (referred to as the air valve) receives clean air at 100mL/min. At any given moment, one of these valves is sending gas into the tee and the mixing chamber, while the other is discarding gas to the vent system. The two valves are actuated by a single control signal so that pulses of vapor and air are alternately sent into the mixing chamber. The relative time periods of these pulses determine the extent of dilution. The mixing chamber mixes the pulses completely so that the vapor stream at its output is of uniform concentration.

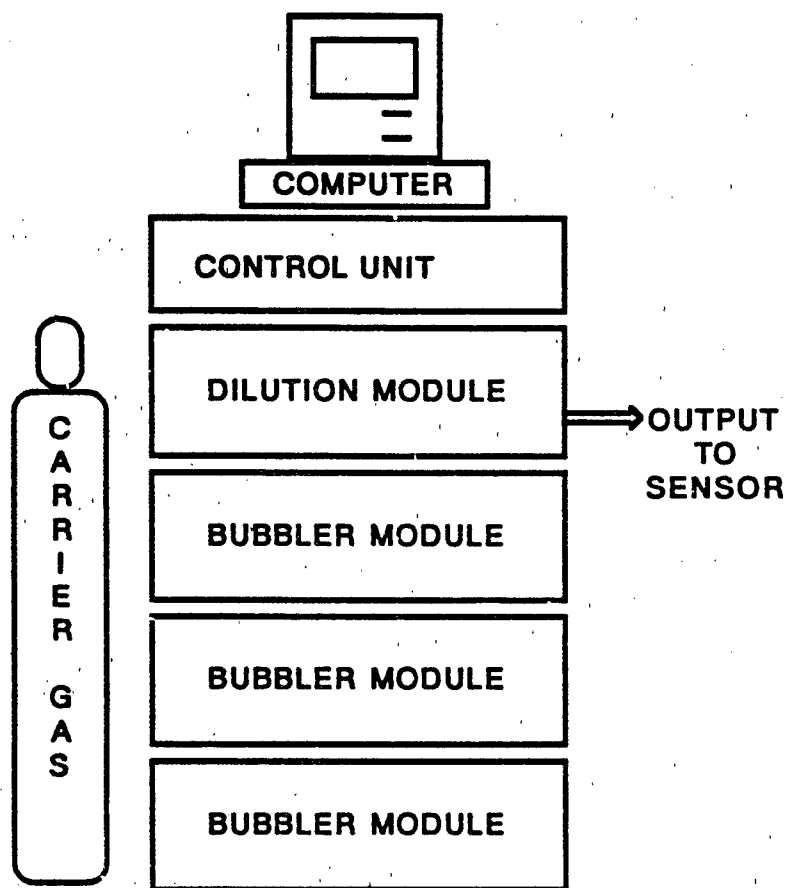


Figure 1. Diagram of the overall vapor generation system.

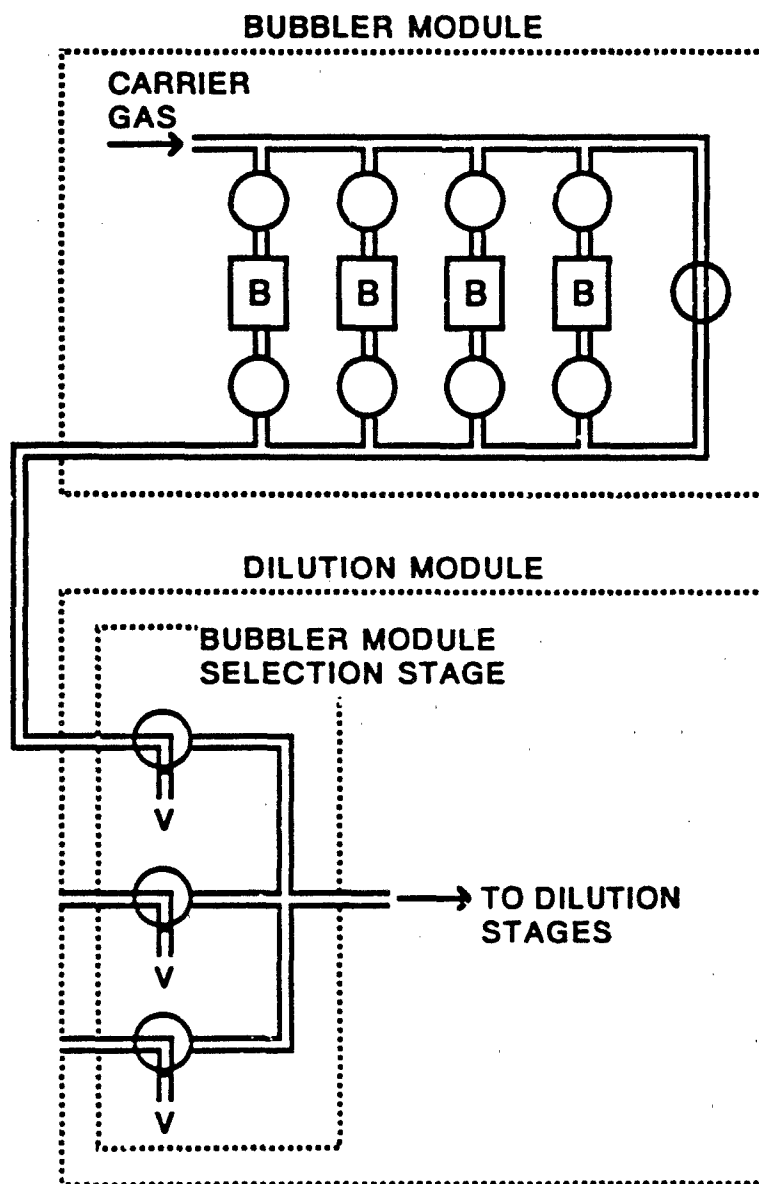


Figure 2. Diagram of the method of selecting a bubbler vapor source. Carrier gas is supplied at 100 mL/min by an electronic mass flow controller. Circles are solenoid valves, B stands for bubbler, and V stands for vent. The valve on the far right of the bubbler module is a bypass valve which is open when no bubbler is selected. When vapor mixtures are generated by pulse width modulation, a mixing chamber is located between the union cross shown and the dilution stages. Valves are shown in their normal(two-way valves) or normally open(three-way valves) positions.

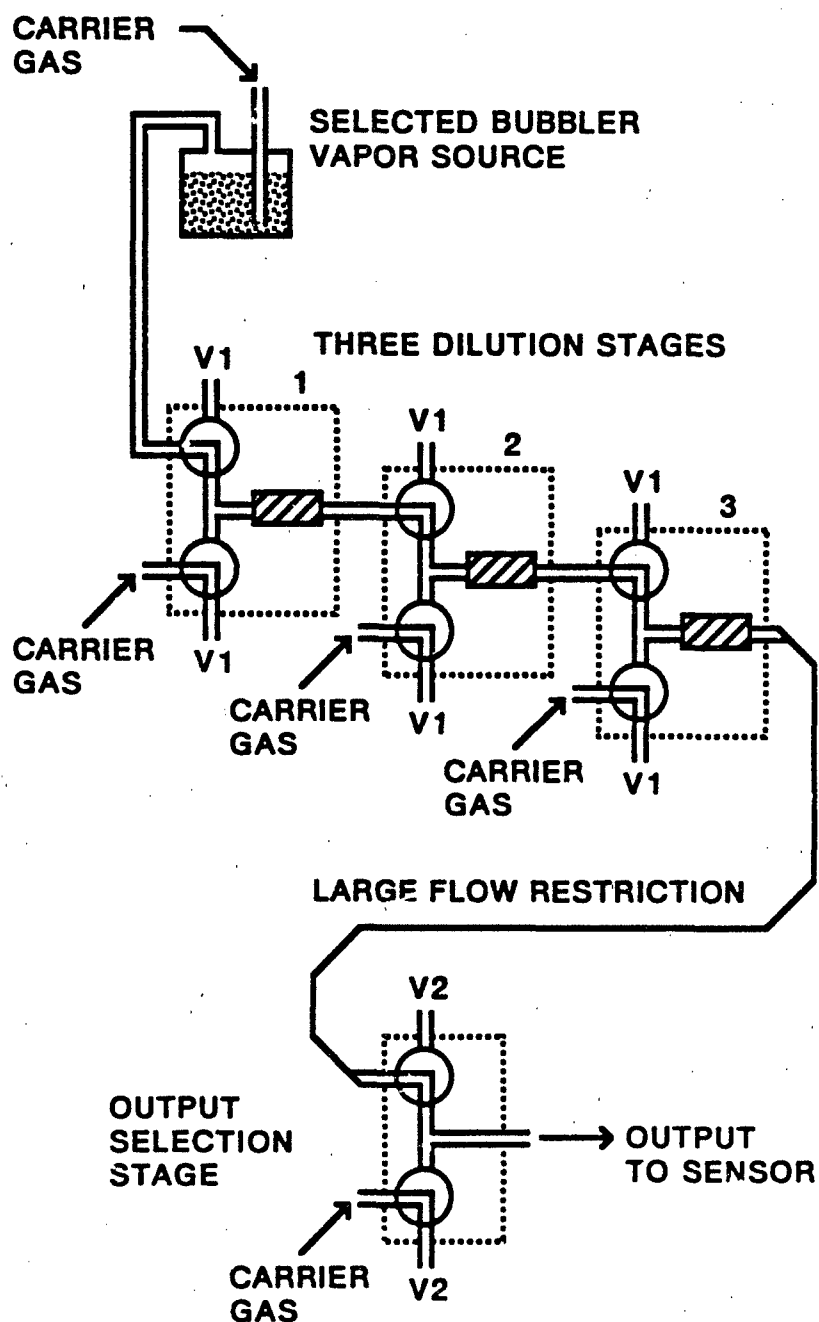


Figure 3. Diagram of the method of dilution. Carrier gas at all points shown is delivered at 100 mL/min by electronic mass flow controllers. Circles are solenoid valves. The diagonally shaded rectangles in each dilution stage are chambers which mix the pulses of vapor and clean carrier gas which are alternately admitted by the preceding pair of solenoid valves. V1 and V2 stand for vents. Valves are shown in their actuated positions, corresponding to the vapor-on portion of the dilution duty cycle, and vapor stream output to the sensor.

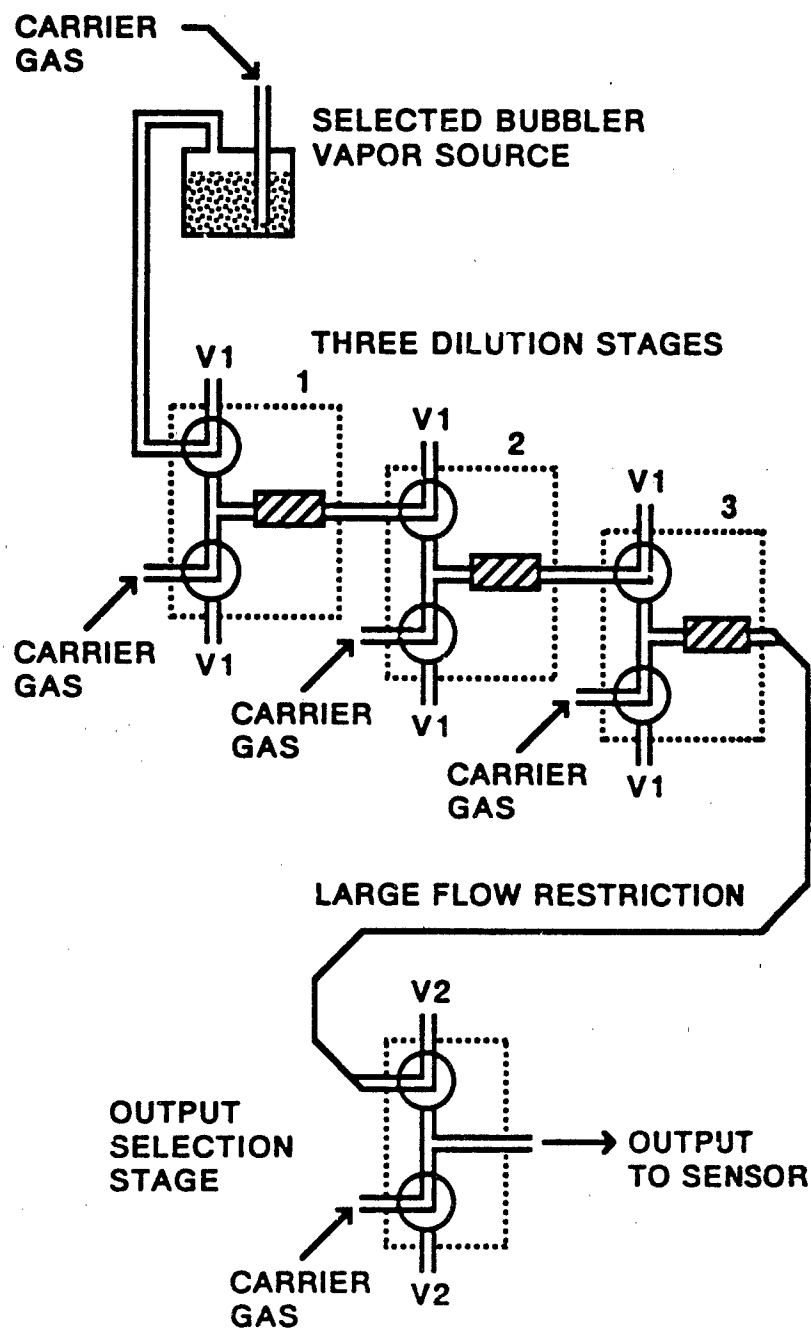


Figure 4. Diagram of the method of dilution with valves shown in their normally open positions. The dilution stage valves are in these positions during the air-on portion of a duty cycle. The output selection stage valves are in these positions during clean air output to the sensor. The valves are also in these positions when the instrument is in its resting state.

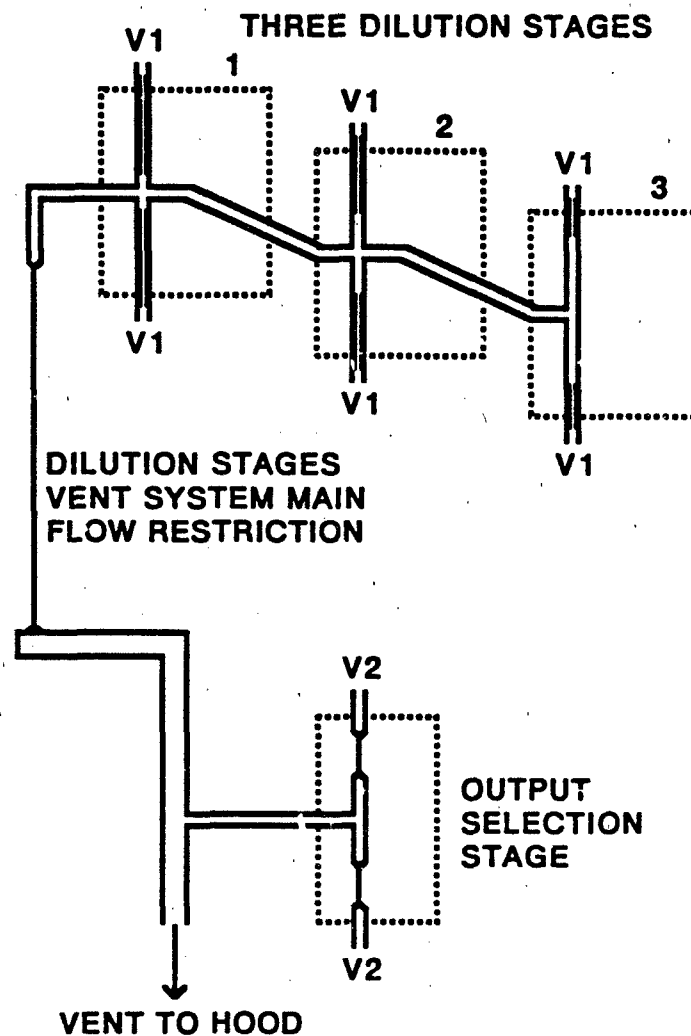


Figure 5. Diagram of the vent systems associated with the dilution stages and output selection stages. V1 and V2 correspond to the positions in Figures 3 and 4. The vents V in Figure 2 also have flow restrictions associated with them which feed into the large bore vent to hood, but are not shown in this figure.

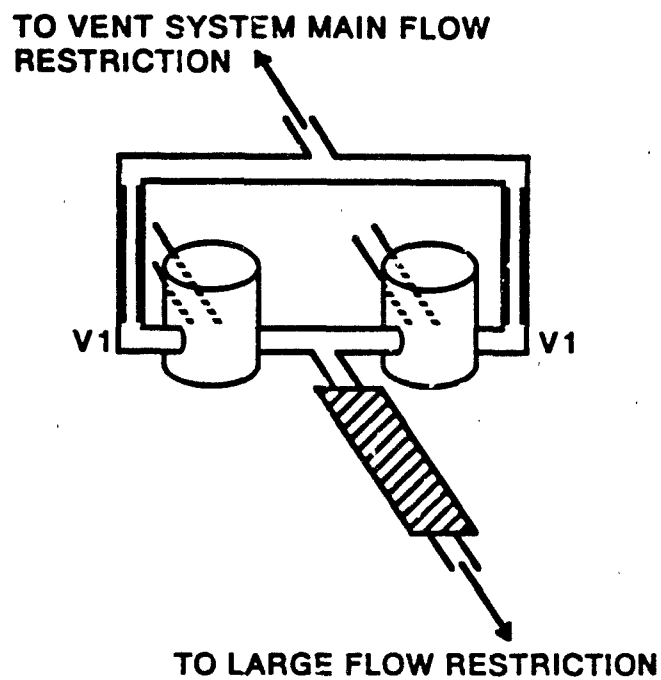


Figure 6. Another view of a dilution stage illustrating how the dilution stage and the vent system are connected. The cylinders are three way solenoid valves whose input connections are behind them. The diagonally shaded parallelogram is a mixing chamber.

The system operates on a 10 sec duty cycle. Thus a dilution to 60% of the input concentration in a given dilution stage is achieved by opening the vapor valve toward the mixer for a 6 sec "vapor-on" period alternately with a 4 sec "air-on" period. Figure 3 illustrates the dilution stage solenoid valves in their actuated positions, which corresponds to the vapor-on portion of a duty cycle. The non-actuated, normally open positions of the dilution stage solenoid valves are shown in Figure 4. The valves will be in these positions during the air-on portion of a duty cycle when all stages are being modulated. For dilutions from no dilution to 2-fold dilution, we modulate only the first dilution stage; the vapor valves of the subsequent dilution stages are actuated continuously so that the vapor stream passes through them to the output selection stage. From 2-fold to 4-fold dilution we modulate the first two stages. For greater than 4-fold dilution we modulate all three stages. For any given dilution, the stages being operated are modulated using identical simultaneous cycles. Thus, for a 125-fold dilution, all three vapor valves are switched on for the first 2 seconds of the duty cycle. Valve switching events have the potential to perturb gas flows; operating the stages simultaneously minimizes the number of such events during a duty cycle.

The critical assumption of this pulse-width modulation method is that the flow rates of the vapor stream and the clean air stream entering a dilution stage are known and constant, and that this condition is maintained even as valves are switched. As the method is implemented in this instrument, the known constant flow rates of the vapor stream and the clean air stream should be identical. It is common experience in many gas flow systems that switching a valve can cause a sudden drop or surge in flows. If such flow perturbations occur in a pulse-width modulation dilution system, the dilution ratio achieved will no longer be dependent solely on the relative time-widths of the pulses. Consider a 1 sec vapor-on period in a stage where the flow drops for an average of 50mL/min for 0.5 sec, with the remaining 0.5 sec at normal 100mL/min flow. The vapor pulse would deliver only 75% of the amount of vapor expected. With three dilution stages in a row, errors can

multiply quickly. The shorter the vapor-on period, the more critical it is that flow perturbations following valve switching be minimized or eliminated. This requires careful design and fine tuning of the vent system into which waste gas streams are discarded.

This example is not an exaggeration. When the vent system is not correctly adjusted, flow drops or surges of much greater magnitude and duration occur. These are observed by placing a rotameter in series with the flow in question. The ball responds to flow perturbations almost instantly, and provides a sensitive indication of flow conditions. (Typical electronic mass flow meters respond too slowly for this purpose.) When the system is carefully adjusted using the approach we describe below, the rotameter ball only briefly "bumps" when a valve switching event occurs.

System Flow Restrictions and Vent System Design. In order to obtain constant flow rates even as dilution stage solenoid valves switch, the pressures at each of the two outlets of a three way solenoid valve must be the same. The pressures at the vapor valve of stage 1 while vapor is being output to a sensor will be considered to explain this principle (see Figure 3). The pressure at the tee outlet (as opposed to the vent outlet) is higher than atmospheric pressure by an amount depending on the flow rate (100mL/min) and flow restrictions between the tee outlet and the final output to the atmosphere. Specifically, flow restrictions leading to pressure differentials are created by the stage 1 mixing chamber, the valves and mixing chambers of stages 2 and 3, the large flow restriction deliberately placed in the flow path, the output selection stage vapor valve, and finally the sensor and its tubing connections. In order for the pressure on the vent outlet of the stage 1 vapor valve to be identical, the flow rate and flow restrictions from that point through the vent system to the final output to atmosphere must produce an identical pressure differential to that in the route from the stage 1 tee through the system and the sensor to the atmosphere. For the system to operate properly, similar conditions must be met for several three-way solenoid valves at various positions in the system, and the

conditions must be met under all the dilution conditions one might select when using the instrument. The design of a vent system to meet these criteria was initially daunting. To help solve this design problem, we first devised a method to measure the relative flow restrictions of the various components of the system. The greatest restriction is caused by the large flow restriction shown in Figures 3 and 4, whose purpose we will now describe.

It is apparent that the flow restriction caused by the sensor and its connection to the instrument output could be a factor in determining the pressures at upstream locations in the dilution system. Different sensor configurations being tested could impose different flow restrictions. Two actions were taken to prevent the necessity of adjusting the vent system before each experiment. First, the large flow restriction (consisting of a length of 1/16" OD Teflon tubing) was designed into the system to render downstream flow restrictions small by comparison. Second, a 6 foot length of 1/8" OD 1/16" ID teflon tubing was connected to the vapor-generation instrument output and adopted as a standard flow restriction which test sensor configurations must match. When a sensor is to be tested, the 6 foot tubing is removed and the sensor inlet and outlet tubes are adjusted so that the flow restriction presented to the instrument output is equivalent to that of the 6 foot tube.

The position of the large flow restriction shown in Figure 3 is important. Given the purpose described above, it might seem logical that it be placed just before the instrument output to the sensor. The vents of all the dilution stage valves and the output stage selection valves might be connected together and sent to the atmosphere via a single suitably adjusted flow restriction. Although having only one vent system flow restriction to adjust appears to be desirable, this configuration was examined and it produced undesirable results which we will not describe in detail here. The importance of correctly adjusting the output selection stage is discussed further below. It is best that the large flow restriction be placed between the dilution stages and the output selection stage, and that the vent system for the dilution stages be adjusted independently of that for the output selection stage. In

this configuration, the dilution process is much less sensitive to events at the output selection stage.

In order to determine a rational scheme for the placement and adjustment of flow restrictions in the vent system, we needed to know the relative restrictions imposed by the various components of the flow system. We used lengths of 1/8" OD 1/16" ID tubing as measures of flow restriction. A tee junction was assembled with 200 mL/min carrier gas flowing into one branch of the tee and out the other two branches. The portion of the flow system to be measured was connected to one outlet, and a length of the 1/8" tubing was connected to the other. This configuration assures that the pressure drops across the system component and the 1/8" tubing are identical. If the length of the 1/8" tubing is adjusted so that the flow rates through both sides are the same, then the flow restrictions are the same and the length of the tubing serves as a measure of the flow restriction of the system component. We refer to this as the "tee" method of measuring flow restrictions.

In practice, adding a flow meter (here we used a Sierra Instruments electronic mass flow meter) imposes an additional flow restriction on the side being measured, so that its flow is actually less than 1/2 the 200 mL/min input to the tee. However, identical readings on each side of the tee remains a valid indication that the two sides are matched. The measurements were further checked by insuring no leaks existed; sealing the end of the side not being measured and obtaining a 200 mL/min flow rate measurement out the other side confirmed the absence of leaks.

Our measurements demonstrated that the mixer of stage 1 plus the valves and mixers of stages 2 and 3 were equivalent to 6" of tubing. The mixer of stage 2 plus the valve and mixer of stage 3 were equivalent to 3.5", and the mixer of stage 1 was equivalent to 1". By comparison, the large flow restriction was equivalent to over 33 feet of tubing.

Therefore, the vent system for the dilution stages was designed as shown in Figure 5. The connections between the vent system and the dilution stages are further clarified by the view of a dilution stage in Figure 6. All dilution stage vents V1 were combined and

directed to a single flow restriction referred to as the dilution stages vent system main flow restriction. This flow restriction was adjusted by a procedure to be described below so that the pressure drop across it (with 300 mL/min. flow) is equivalent to that from the beginning of the large flow restriction through the output selection stage and the 6 foot 1/8" OD tube attached to the instrument output (with 100 mL/min flow). (The 6 foot tube is not shown in any Figure; it is connected to the 'Output to Sensor' shown in Figures 1,3, and 4). Though this may have been trivial, we further accounted for differences in the positions of the V1 vents of the three dilution stages by press-fitting lengths of 1/8" OD 1/16" ID tubing into the 1/4" OD 1/8" ID tubing connected to the solenoid valve vent outlets. Pieces of 1/8" tubing of 6", 3.5", and 1" lengths were press fit into the outlets of the stage 1, 2 and 3 valves respectively, corresponding to the flow restrictions measured above by the "tee" method.

The major flow restriction of the vent system for the dilution stages was adjusted (i.e. the dilution system was "balanced") with the valves of the dilution stages and the output selection stage actuated as shown in Figure 3. A carrier gas flow of 100 mL/min originated in a selected bubbler module, with no bubbler selected. This gas passed through the dilution stages and the output selection stage to vapor generation instrument output, and on through the attached 6 foot tube to the atmosphere. The 100 mL/min carrier gas streams going into each air valve of the three dilution stages proceed out their respective V1 vents and join to pass through the dilution stages vent system main flow restriction.

Flow conditions were observed by placing a rotameter in series between the tee and the mixing chamber of dilution stage 3. The rotameter adds a flow restriction which we had determined to be equivalent to 2.5 feet of 1/8" OD tubing when 100 mL/min pass through it. Therefore, 2.5 feet were removed from the 6 feet of tubing on the instrument output.

With the rotameter in place, it is a simple matter to observe the effect of switching pairs of solenoid valves in the dilution stages. The length of the dilution stages vent system

main flow restriction (1/16" OD stainless steel tubing connected with brass ferrules to prevent tubing constriction) was adjusted until switching a pair of valves causes only a momentary bump of the rotameter ball. With proper adjustment, switching one or more pairs of valves produces momentary bumps of less than 10% lasting 0.2 sec or less. The rotameter can then be removed. We have rechecked the dilution vent system balance periodically over many months, and have never needed to readjust it. *This method of directly observing the flow conditions during dilution operations provides a high degree of confidence that the dilutions are performed exactly in the manner intended. Conversely, if significant flow perturbations are observed during dilution operations, it follows that the diluted concentration which is actually generated will not be identical to that predicted by the relative time-widths of the pulses alone.*

Note that the position of the rotameter is carefully chosen to provide the best sensitivity to balance at the dilution stages. It is more convenient to place the rotameter on the instrument output, but one loses sensitivity to events at the dilution stages because of the large flow restriction in between.

It is also necessary to separately adjust flow restrictions in the vents V2 (Figures 3 and 4) of the output selection stage. Although it is not obvious in the figures, the flow restriction presented to the instrument output when a test sensor (or the aforementioned 6 foot length of tubing) is attached can be significant. When the instrument is delivering clean air at the output, the diluted vapor stream is discarded into the vents. The flow restriction the vapor stream encounters in the vent system must be the same as that which it encounters when it is delivered out the instrument through the test sensor to the atmosphere. If the output selection stage vent system flow restrictions are not correct, then the pressures upstream at the dilution stages will not be correctly balanced while the vapor stream is discarded to vent. (Recall that the dilution stages were balanced with the vapor stream being output through the 6 foot tube.) Thus, while clean air is output to the sensor, the now unbalanced dilution stages equilibrate to a somewhat different vapor concentration

than the one intended. On switching the instrument to vapor output, the dead volume containing this different concentration is delivered to the sensor until the instrument re-equilibrates and delivers the concentration which is generated under properly balanced conditions. This effect can be easily observed using standard thermal conductivity or photo ionization detectors on the instrument output; two detector response levels are observed during a single vapor output period. (It can also be observed using various experimental microsensors, in which case the odd effect should not be incorrectly attributed to a peculiarity of the experimental sensor.) This type of problem was particularly noticeable when the output selection stage was placed before the large flow restriction, as alluded to briefly above.

Therefore, the output selection stage and large flow restriction were arranged as shown in Figures 3 and 4, and the vents for the output selection stage were adjusted with flow restrictions shown in the vent outlets V2 of the two output selection stage solenoids, as shown in Figure 5. A logical alternative arrangement would be to combine the two V2 vents with a tee and place a single flow restriction in the third leg of the tee.

Finally, flow restrictions must be placed in the vents V (see figure 2) of the bubbler module selection stage. For experiments where a single vapor is utilized, the relevant bubbler module selection valve is open and remains open for the entire experiment, so adjustment of the vent V flow restriction is not critical. However, if a vapor mixture is to be prepared by selecting two bubblers from two bubbler modules, and mixing them by pulse-width modulation, then vent V restriction adjustment is critical. The correct flow restriction can be determined by the "tee" measurement technique described above, and double checked by using a rotameter.

When vapor mixtures are prepared, a mixing chamber is placed between the union cross in Figure 2 and the dilution stages. However, when mixtures are not being prepared, this chamber creates unnecessary dead volume and surface area to retain vapors, and we prefer to remove it.

Calibration and Dilution of Bubbler Vapors. The mass flow rates of the vapors from the bubblers can be calibrated gravimetrically by quantitatively capturing the vapor on a tared sorbent tube. We utilize tubes packed with activated charcoal and molecular sieves in series, and calibrate the saturated (at 15°C) bubbler streams at no dilution. For bubbler liquids with low saturated vapor pressures, the saturated vapor concentration is calculated from the vapor mass flow rate divided by the carrier gas volumetric flow rate.

$$\text{concn} = \frac{\text{vapor mass flow rate}}{\text{carrier gas volumetric flow rate}} \quad (1)$$

When the bubbler liquid has a high saturation vapor pressure, the actual volumetric flow rate of the saturated vapor stream must include the volumetric flow rate of the vapor as well as that of the carrier gas.

$$\text{concn} = \frac{\text{vapor mass flow rate}}{(\text{carrier gas volumetric flow rate} + \text{vapor volumetric flow rate})} \quad (2)$$

If the vapor's volumetric flow rate included in eq 2 is ignored as in eq. 1, then the calculated concentration from a liquid with a high saturation vapor pressure will be somewhat greater than the actual concentration. Table I lists the vapor pressures of several organic liquids at 15°C and the volumetric flow rates of vapor expected from bubblers containing them, assuming a 100 mL/min carrier gas flow rate.

The dilution of vapor streams from bubblers with low saturation vapor pressure liquids is straightforward. All carrier gas flow controllers are set to the same flow rate, assumed to be 100 mL/min for this discussion. Dilutions are performed just as described in previous sections. The resulting vapor concentration is simply calculated from the calibrated concentration from the bubbler times the dilutions at each dilution stage.

Table I. Vapor Pressures and Volumetric Flow Rates for Some Typical Organic Vapors.

Vapor	Vapor Pressure^a (15°C) torr	Volumetric Flow Rate^b mL/min
n-butanol	4.0	.5
toluene	16.2	2.2
2-propanol	23.0	3.1
isooctane	28.2	3.8
1,2-dichloroethane	47.5	6.7
2-butanone	59.8	8.5
dichloromethane	274	56

^aCalculated from data in the CRC Handbook of Chemistry and Physics

^bAssuming a 100 mL/min flow of carrier gas into a bubbler.

However, if the bubbler contains a liquid with a high saturation vapor pressure, dilution by the pulse-width modulation method requires special care. Recall the critical assumption of the pulse-width modulation method: the volumetric flow rates of the vapor stream and the dilution air stream must be identical. This condition was met in the case considered in the previous paragraph; the volumetric flow rate of vapor from a bubbler liquid with a low saturation vapor pressure is negligible relative to the carrier gas flow rate. However, many liquids one might want to generate vapors from are volatile, and the resulting bubbler vapor volumetric flow rates are not negligible, as seen in Table 1. If carrier gas flow rates remain at 100 mL/min, then the total vapor stream flow rate entering the vapor valve of the first dilution stage will exceed the clean air flow rate into the corresponding air valve. This condition violates the critical assumption of the pulse-width modulation method. Pulses of vapor during a dilution will be too large, and the vapor concentration actually achieved will be higher than intended (i.e. as calculated from the saturated vapor concentration times the dilutions at each dilution stage as determined by the timing of their duty cycles). For modest dilutions, this difference is small. However, it becomes surprisingly significant for vapor streams from high vapor pressure liquids being diluted in all three dilution stages.

Clearly, the rigorous approach in handling vapors from liquids with significant vapor pressures is to lower the volumetric flow rate of the carrier gas into the bubbler so that the total volumetric flow rate out of the bubbler is the desired 100mL/min. The configuration in Figure 2 is somewhat awkward in that a single carrier gas flow controller is present in each bubbler module, and its flow rate is pre-set manually. If the four bubblers in a module have diverse vapor pressures, no single pre-set flow rate will be appropriate for all of them. To achieve high dilutions and still obtain accurate results from all bubblers, the flow controller flow rate would have to be manually readjusted in between experiments.

Two alternative hardware configurations would alleviate these difficulties. First, a carrier gas flow controller could be dedicated to each bubbler and its flow rate could be adjusted appropriately for the liquid in that bubbler. This approach would be costly using electronic flow controllers for a total of twelve bubblers. The second alternative is to retain a single electronic flow controller in each bubbler module, but include hardware (e.g. digital to analog converters) in the control unit so that carrier gas flow rates can be programmed electronically. At the start of each experiment, the bubbler module carrier gas flow rate could be set to a level appropriate for the particular bubbler chosen. Our VG7000 vapor generator is not presently equipped for either of these alternative methods, but they clearly could be included in future instrument modifications.

Using the configuration in Figure 2 with a single carrier gas flow controller in each bubbler module whose flow rate is pre-set manually, we can suggest two other options. These options are useful when the test sensor is to be screened against a variety of vapors and high dilutions are not necessary. First, note that no problem is encountered if no dilution is performed and saturated vapor concentrations are calculated from calibrated mass flow rates via eq 2. Second, we have calculated that at a dilution to 25% of the saturated concentration, using 5:5 duty cycles in stages 1 and 2, the known errors compensate. In this option, all saturated vapor concentrations are calculated by eq 1, regardless of bubbler vapor pressure. Then the saturated vapor concentration is divided by four to get the diluted concentration. For vapors with high vapor pressures, the actual saturated concentration is less than that calculated, but the actual dilution yields concentrations higher than calculated. These errors compensate and the vapor concentration actually achieved at the instrument output is very close to that calculated in this manner at this dilution. Although this option limits one to a single dilution level (to 25%), it works regardless of the bubbler liquid's vapor pressure. One can screen a test sensor against a wide variety of vapors without changing the carrier gas flow rate from its preset 100mL/min.

System Use and Flushing. Thus far the discussion has focused entirely on factors influencing the correct operation of the pulse-width modulation method. One additional aspect of the pulse-width modulation method that merits attention is the requirement to adequately flush the system out after an experiment. This is necessary with all vapor systems, but it is particularly important with this method because of the volumes and surfaces of the mixing chambers. Vapor adsorbed on surfaces will desorb and bleed into the carrier gas at low concentrations. Adequate flushing time is required in between experiments to insure that subsequent experiments are not contaminated by the previous vapors.

We have adopted a number of practices to insure adequate system flushing, including control experiments before each vapor experiment. To describe these control experiments, we must first describe normal instrument operations.

Instrument functions are executed by a program running in the control unit (see Figure 1). The control unit sends signals to the dilution and bubbler modules to operate solenoid valves. It must receive serial input from a microcomputer which specifies the parameters for one experiment. The program executes that experiment; at its completion, the program is ready for parameters for the next experiment. If sequences of vapor experiments are to be executed, the microcomputer must provide the control unit with the parameters for each experiment when the control unit is ready for them.

The VG7000 came equipped with software to set up sequences of vapor experiments. However, we found it more useful to communicate with the control unit using a commercial communications program (Smartcom II on the Macintosh). This allowed us more authority over dilution timing, system flushing, and control experiments. Sequences of vapor experiments are easily programmed using the macro or "autopilot" capability of the communications program to read text files from disk and communicate their contents over the serial line at pre-programmed intervals. The text files contain the parameters for an experiment.

The parameters for an experiment instruct the control unit to select a bubbler module, a bubbler in that module, and specify the duty cycles for each dilution stage. In addition the timing of the output selection stage is specified. This timing begins with a warm up period to equilibrate the vapor stream. During this period the vapor stream is discarded to vent at the output selection stage while clean air is delivered to the test sensor. Then a time period is specified for delivery of the vapor stream to the sensor, followed by another period of clean air output. Cycles of vapor/clean air can be repeated. At the completion of the experiment, the bubbler and bubbler modules are de-selected, all dilution stops, and clean air is delivered at the output.

Before each vapor experiment, we execute a control experiment which is identical except that no bubbler is selected. *The same bubbler module is selected, so that carrier gas flows follow identical pathways in the control and vapor experiments.* The warm-up period provides flushing time, and we monitor the sensor as usual during the output cycles. If no response is seen, then the system is adequately flushed and a response in the subsequent experiment is certain to be due to vapor from the bubbler selected.

When an experiment or sequence of experiments is complete, the control unit leaves the instrument in a resting state. No bubbler modules are selected. In this state there is no carrier gas flow in the pathway between the bubbler module selection stage and the vapor valve of the first dilution stage (see Figures 2 and 4). The vapor from the previous experiment remains in this section indefinitely. Therefore we send a final set of parameters over the serial line instructing the control unit to select a bubbler module (but no bubbler), providing carrier gas to flush this section of the system. In this configuration, all pathways are continuously flushed.

Final Remarks. The discussion above has focused on the principles of operation, and has not indicated, for example, the warm up periods and flushing times required with this instrument. These will vary with the particular vapors being used; less volatile vapors will take longer to equilibrate and to flush out than more volatile vapors. Analysts should determine times appropriate for their own instruments, the vapors they use, and the types of experiments they want to execute. Because we use a wide variety of vapors, we normally err on the side of caution choosing long warm up periods of 30-45 minutes. Since control experiments are run identically, long warm up periods provide adequate flushing times for most volatile organic vapors.

The pulse-width modulation method as designed into this instrument by Microsensor Systems is a novel method to dilute vapor streams using a minimum of carrier gas. Diluting a 100 mL/min vapor stream to a thousandth of its source concentration requires only an additional 300 mL/min of carrier gas, compared to the nearly 100,000 mL/min that would be required by a simple flow system. In addition, the volumetric flow rate of the instrument output is constant regardless of the dilution. On the other hand, the dilution of vapor streams by simple flow methods is quite straightforward, especially when electronic flow controllers are utilized to regulate carrier gas flow rates. The pulse-width modulation method dilutes in ratios determined by duty cycle timing only if the flow rates of the vapor streams and carrier gas streams are identical and constant. This critical assumption of this method is worth recognizing and respecting. It was this aspect of pulse-width modulation that prompted us to describe the method in this note.

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13. ABSTRACT (Maximum 200 words) <p>→ A pulse-width modulation method for the dilution of calibrated vapor streams is described. The critical assumption of the method is that the flow rates of the vapor and clean carrier gas streams being modulated are identical and constant, and that this condition is maintained even as valves are actuated. Under these conditions, dilution occurs in ratios determined by duty cycle timing. Flow perturbations occurring on valve-actuation can significantly influence whether dilutions achieved match those calculated by duty cycle timing. Methods to eliminate such perturbations by careful placement of flow restrictions in the vent system are described. The effects of organic liquid vapor pressures on this dilution method are also described.</p>				
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